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(54) Title: PROCESS FOR THE PRODUCTION OF BUTANEDIOL

(57) Abstract

Process for the production of 1,4–Butanediol by vapour phase catalytic hydrogenation of gamma–butyrolactone, maleic and/or succinic anhydride methyl esters or mixtures of gamma–butyrolactone and maleic and/or succinic anhydride esters, characterised by the fact that, in the operating conditions described in the process, by feeding hydrogen gas containing carbon monoxide to the reaction, a concomitant production of synthesis methanol is obtained, and conversion values relating to methanol production are improved.

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Process for the production of Butanediol.

Description.

The present invention relates to a process for the production of 1,4-butanediol by vapour phase flow catalytic hydrogenation of gamma-butyrolactone, succinic or maleic anhydride methyl esters, or mixtures thereof, wherein the hydrogen flow is enriched with CO, so as to accomplish an extra production of synthesis methanol, with a consequent increase in the yield of the final product.

It is known from the prior art that there exist many processes for the preparation of butanediol using dicarboxylic acid esters with four carbon atoms as starting materials.

In USSR Patent N°400,567 a copper chromite catalysed liquid phase conversion of esters into BDO at temperatures ranging between 280 and 300°C and 300 bar pressure is given.

In US Patent N°4,613,707 a conversion of diethylsuccinate into BDO at 200°C T and 135 bar pressure with a mainly copper and aluminium borate catalyst is given.

In US Patent N°2,079,414 a vapour phase hydrogenation of esters is given, on a copper chromite type catalyst and temperatures ranging between 300 and 400°C.

In US Patent n° 2,040,944 a broad description of both liquid and vapour phase ester hydrogenations is given, using copper chromite catalysts. In one example, a liquid phase butyl succinate hydrogenation at 207 bars is described.

In US Patents n°'s 4,584,419 and 4,751,334, assigned to Davy Mc Kee Ltd. (U.K.) processes for the large scale production of BDO are described and they involve four carbon dicarboxylic acid ester hydrogenations.

The operating conditions of the hydrogenations claimed in the patents assigned to Davy McKee Ltd. are pressures ranging between 25 and 75 bars, and temperatures between 150° and 240 °C, in the presence of a stabilised cuprous chromite type catalyst in its reduced form.

Moreover in the latter patent it is stated that the process which is claimed in it yields a 79.3% conversion into the desired product, after the first stage.

There is no indication of the overall conversion, but it is not at all unfair to be sure that it is somewhat lower than the above value.

Likewise, a 78.3% overall conversion is obtained in the process claimed in the former patent.

Clearly, as the above values hold on an industrial scale, they leave much room for substantial improvements.

Aim of the present invention is therefore to propose a process which allows much higher conversion rates, therefore increases the profitability of its application to the plant scale.

Another aim of the present invention is that of proposing a methodology for the contemporaneous production of BDO and methanol (MOH) operating in specific conditions and on suitable catalysts.

The above aims are accomplished by a process for the production of 1,4-butanediol by vapour phase selective hydrogenation of gamma-butyrolactone, maleic or succinic anhydride methyl esters or mixtures of gamma-butyrolactone with the esters thereof, characterised by the fact that synthesis methanol is coproduced by feeding hydrogen gas enriched with carbon monoxide to the reaction.

According to the process of the present invention, methyl dicarboxylic acid esters with four carbon atoms, e.g. dimethylmaleate (DMM) or dimethylsuccinate (DMS), gamma butyrolactone (GBL), or mixtures of GBL with the esters thereof, are utilised as starting materials for the production of BDO.

Methanol synthesis is accomplished by feeding carbon monoxide together with hydrogen gas. The reaction by which BDO forms thanks to the hydrogenation of an ester like DMS for example, is given by the following equation:

(A) $CH_3\text{-}O\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}O\text{-}CH_3 + 4H_2 \rightarrow 2CH_3OH + OH(CH_2)_4OH$

The MOH synthesis reaction is given by the following equation:

(B) $CO + 2H_2 \rightarrow CH_3OH$

MOH that forms in reaction (A) is recovered to be fed to an esterification unit .

However from a practical viewpoint, part of the MOH is lost either literally or in the form of by-products. MOH real losses, about 0.1 to 0.3 mols for each mol of BDO produced, may even be compensated by MOH formation according to reaction (B), this making the production unit completely self-sufficient in terms of MOH.

The most important aspect is the neat improvement given by the process object of the present invention in so far as the yield of reaction (A) is concerned, more than its self-sufficiency in terms of MOH consumption, the latter being nevertheless a not unimportant factor.

Surprisingly, the MOH synthesised which adds up to the MOH produced in reaction (A) is not of any hindrance to the BDO synthesis reaction as it would be expected to be. Instead it results to have a remarkably positive effect on the conversion of the ester and/or GBL of the shot.

The surprising observation stated above may be explained by dint of the protective action exerted onto the active sites of the catalyst by the methanol synthesis.

It may be significant that the catalyst employed in the hydrogenation reaction is of either the exact same or similar type as that employed in methanol synthesis, e.g. of the copper-zinc oxide, or cuprous chromite type, this ensuring a compatibility and ease of coexistence of the two reactons in the same vessel.

In the process which is object of the present invention, the typical operating conditions for this reaction are as follows:

Reaction type:	adiabatic
Molar ratio between H_2 and ester:	from 200 to 800, preferably from 200 to 500
Molar ratio between CO and	

shot ester:	from 0.1 to 1.0 preferably from 0.2 to 0.4
Operating pressure:	from 75 to 120 bars, preferably from 80 to 100 bars
Operating temperature:	from 170 to 230°C preferably from 190° to 210 °C
Type of catalyst:	Copper/Zinc oxide or cuprous chromite
Liquid Hourly Space Velocity:	from 0.1 to 1.0 hr^{-1}, and averagely from 0,3 to 0.5 hr^{-1}

These and other features will be more readily apparent from the following description of a preferred not limiting embodiment of the invention with reference to the accompanying drawing in which a scheme (Fig. 1) of the production process is shown.

The following operating conditions refer to a starting material made up of a mixture of GBL and DMS in 70:30 proportions by weight.

The feed mixture (Line 1) is fed to vapouriser 3, together with a liquid recycle mixture (Line 2), that contains GBL from fractionation unit 22. In vapouriser 3 both the feed (Line 1) and the recycle (Line 2) come to contact with a hot hydrogen stream (Line 4), and they vapourise. In the gas stream coming out of the vapouriser (Line 5) the molar ratio between hydrogen and ester is 300:1, the molar ratio between CO and ester is 0.2, temperature is 190°C and pressure is 80 ATE.

Such stream feeds Stage I of reaction 6 where there is a copper-zinc oxide type catalyst with a surface area never any smaller than 40 m^2g^{-1}.

At the inlet of Stage II in reaction 7, temperature is taken down to approx. 190°C by injection of a cold hydrogen stream (Line 7). Overall Liquid Hourly Space Velocity in the two reaction stages is 0.35 hr^{-1}.

At the inlet of Stage II in reaction 8, DMS conversion results to be higher than 98%, while GBL conversion in the feed is higher than 91%.

The overall average conversion value works out to be as high as 93%.

By-products obtained in the process consist of tetrahydrofuran (THF)-about 6% on a molar base with respect to the BDO produced.

Selectivity of the reaction is approx. 99% with respect to the overall amount of BDO and THF produced.

The high molar ratio between hydrogen and carbon monoxide favours the occurrence of methanol synthesis with stepwise conversion values higher than 90%.

The effluent from the reactor (Line 9) cools down in exchanger 10, letting heat to the recycle hydrogen rich stream, and in exchanger 11. Eventually it feeds (Line 20) separator 12 where the condensed organic phase separates from the hydrogen rich gaseous phase.

The gaseous phase coming out of separator 12 (Line 13) is compressed by compressor 14 to be recycled into the reaction system.

A small fraction of the recycle gas is purged (Line 15) to minimise the accumulation of inert materials.

The compressed gas (Line 16) and the feed hydrogen and carbon monoxide (Line 17), partly (Line 7) blend with the effluents from the first stage of reaction 6, and partly (Line 18) pre-heat in exchanger 10 and in terminal heater 19, to subsequently feed (Line 4) vapouriser 3.

The liquid phase coming out of separator 12 feeds (Line 21) product fractionation unit 22, where THF (Line 23), MOH (Line 24), water and light organic by-

products (Line 25), an unconverted GBL rich organic fraction (Line 2) bound to be recycled for hydrogenation, heavy organic by-products (Line 26) and BDO (Line 27) separate.

The innovative aspect of the process object of the present invention is better emphasised by a comparison of its performances of which above with those obtained carrying out the hydrogenation with the same shot and operating conditions, nevertheless without streaming any carbon monoxide gas.

It was found that without carbon monoxide, hence without any MOH synthesis, keeping the same high selectivity values, the overall conversion of GBL to DMS decreases from the 93% mark, obtained when feeding carbon monoxide, to approx. 84 %.

The lower conversion rates entice higher investment and production costs, both in the hydrogenation section, and in the subsequent distillation sections where the unconverted fractions bound to be recycled for hydrogenation are separated.

CLAIMS

1. A process for the production of 1,4-butanediol by vapour phase selective hydrogenation of gamma-butyrolactone, maleic or succinic anhydride methyl esters or mixtures of gamma-butyrolactone with the esters thereof, characterised by the fact that synthesis methanol is coproduced by feeding hydrogen gas enriched with carbon monoxide to the reaction.

2. A process according to claim 1, characterised in that the molar ratio between carbon monoxide and shot ester ranges between 0.1 and 1.0

3. A process according to claims 1 and 2, characterised in that the hydrogen to shot ester molar ratio ranges between 200 and 800.

4. A process according to claims 1,2 and 3, characterised in that its operating pressure ranges between 75 and 100 bars, and its operating temperature ranges between 170° and 230°C.

5. A process according to claims 1,2,3 and 4, characterised in that the hydrogenation catalyst is of the copper-zinc oxide or stabilised cuprous chromite type,with surface area never any smaller than 40 m^2g^{-1}.

6. A process according to claim 5, characterised in that the vapour phase mixture containing shot hydrogen and ester contacts the catalyst

with a liquid hourly space velocity ranging between 0.1 and 1.0 hr^{-1}.

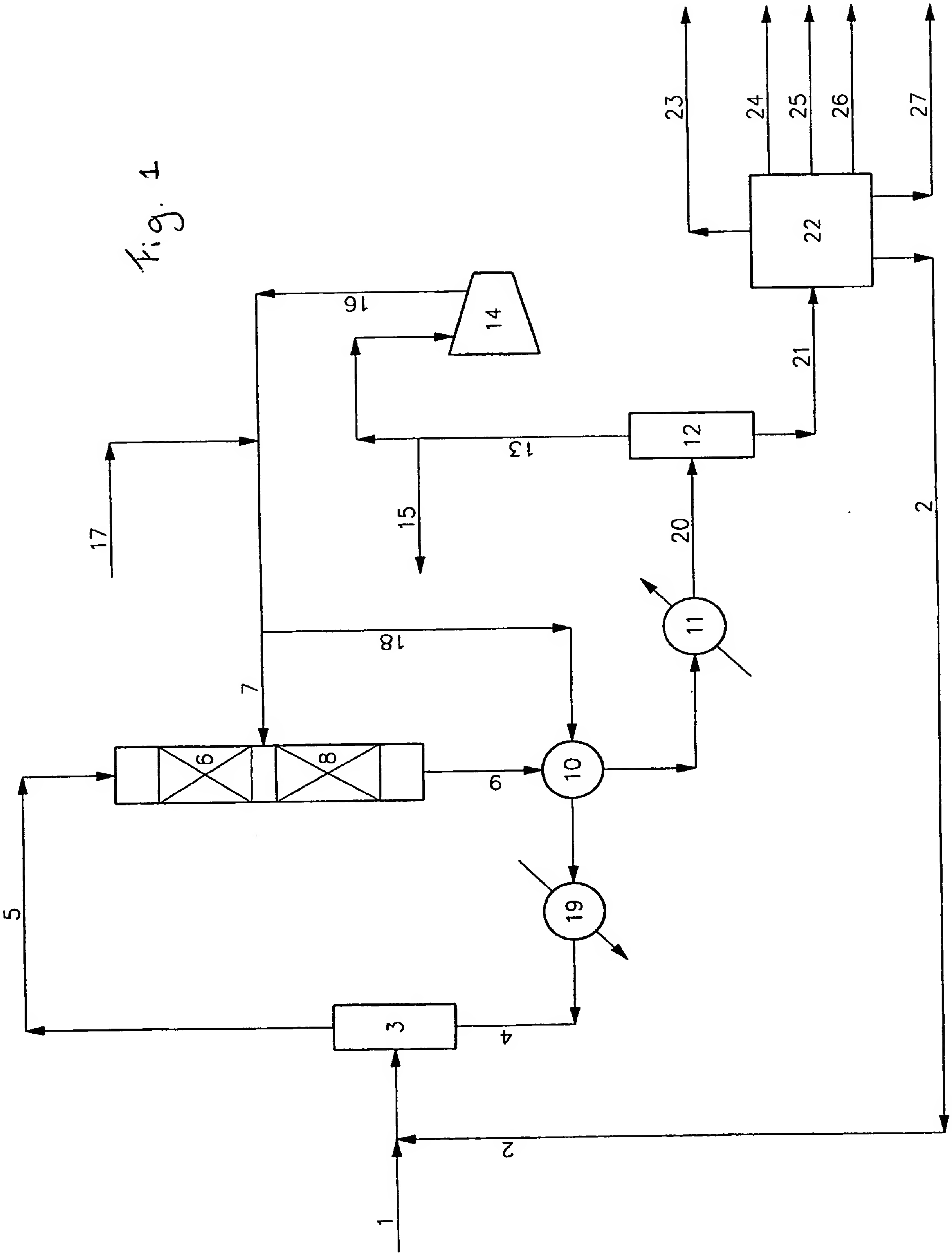

Fig. 1

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C29/136 C07C31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 584 419 A (SHARIF MOHAMMAD ET AL) 22 April 1986 (1986-04-22) cited in the application column 4, line 42 - line 44; claim 1; example 1; table IV	1-6
Y	EP 0 722 923 A (STANDARD OIL CO OHIO) 24 July 1996 (1996-07-24) page 3, line 19 - line 21; claims 1-3	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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